MICROKINETIC MODELING OF TOLUENE AND O-XYLENE HYDROGENATION ON PT CATALYST

Tapan Bera, Joris W. Thybaut and Guy B. Marin
Ghent University, Ghent, Belgium.

Abstract

The Single-Event MicroKinetic (SEMK) methodology, which had been successfully applied to benzene hydrogenation, has now been extended towards substituted aromatics, i.e., toluene and o-xylene. In addition to the number of unsaturated nearest neighbor carbon atoms, H-atom addition rate coefficients were assumed to depend on the carbon atom type, i.e., secondary or tertiary. A simultaneous regression of the SEMK model to an experimental data set consisting of 39 toluene and 37 o-xylene hydrogenation experiments resulted in activation energies of H-additions to tertiary carbon atoms that are 11 kJ mol^{-1} higher than to secondary carbon atoms. This can be related to the steric hindrance experienced during H addition to a carbon atom bearing a substituent.

Introduction

Both quality and environmental concerns continue to impose stringent restrictions on the aromatic content of transportation fuels [1]. Hydrocracking of heavier petroleum fractions is one of the most important processes in the refining industry for the production of high quality fuels. Typical hydrocracking feeds contain a significant aromatic fraction. In this work, the hydrogenation of aromatics is studied as part of hydrocracking process.

Kinetic models are very important for process and catalyst design, development and optimization. In this work, the single-event microkinetic (SEMK) concept is used for the determination of aromatic hydrogenation kinetics which ensures feedstock independence of kinetic parameters [2]. The fundamental SEMK model is based on elementary steps without postulating a rate-determining step. In contrast to typical literature reported kinetics models for aromatic hydrogenation, it accounts for the position in which the H atoms are added to the aromatic ring and, hence, for all possible surface species. It provides a unique insight in potential dominant reaction pathways, most abundant surface intermediates as well as the identification of a rate-determining step. While originally applied to thermal [3] and acid catalyzed reactions [2,4], the SEMK methodology has recently successfully applied to benzene hydrogenation [5] and is now being extended towards substituted aromatics, i.e., toluene and o-xylene.

Procedures

Toluene and o-xylene hydrogenation experiments have been performed in a gas phase continuous stirred tank reactor at temperatures in the range of 423–498 K, H_2 inlet partial pressures of 100–600 kPa and aromatic inlet partial pressures of 10–60 kPa on a 0.5%Pt/H-ZSM22 catalyst. The total pressure was in the range 1-3 MPa, while space times from 22 to 90 kg s mol^{-1} have been used. Pt/H-ZSM-22 was selected as catalyst as it is expected to limit secondary acid catalyzed reactions by its shape selective properties. At these conditions intrinsic kinetics are measured as the maximum Weisz moduli were calculated at 10^{-2} [6,7]. The model has been regressed to an experimental toluene and o-xylene hydrogenation data set consisting of 39 and 37 data points respectively.

A Levenberg-Marquardt algorithm [8] as implemented in the ODRPACK routine was used for parameter estimation during simultaneous regression of toluene and o-xylene hydrogenation data [9]. An objective function defined as the sum of squared residuals between the observed and calculated outlet methylcyclohexane and 1,2-dimethylcyclohexane flow rates, is minimized. The minimization occurs through adjustment of the model parameter vector **b** which approximates the real parameter vector **β** at the minimal value of the objective function:

$$SSQ = \sum_{j=1}^{nob} (F_{CA,j} - \hat{F}_{CA,j})^2 \xrightarrow{b} \min$$

Here $F_{CA,j}$ is the experimental outlet molar flow rate for the saturated cycloalkane produced by hydrogenation of corresponding aromatic compound of the j^{th} experiment and $\hat{F}_{CA,j}$ is the corresponding model calculated value.

The cycloalkane outlet flow rate is calculated by solving the non linear equation:

$$\hat{F}_{CA,j} - \hat{R}_{CA,j}\ T, p_t, \hat{F}_{CA,j}, F_A^0\ W_j = 0$$

i.e., via the mass balance for saturated cycloalkane over the reactor, if the latter is not fed. The saturated cycloalkane net production rate is calculated from the kinetic model, which gives rise to a set of algebraic equations. These algebraic equations are solved simultaneously with the mass balance equation using a hybrid Powell method [10].

Experimental results

The hydrogenation of toluene and o-xylene yielded methylcyclohexane and dimethylcyclohexane as the main product in the investigated range of operating conditions. The effect of the operating conditions on the aromatic hydrogenation behavior is consistent with the literature [5,1114]. In particular a maximum is observed in the hydrogenation conversion as a function of the temperature, see Figure 1. At a certain temperature, the increase of the hydrogenation rate coefficient with the temperature is overcompensated by the decrease of the surface concentrations of the partially hydrogenated species [5,11].

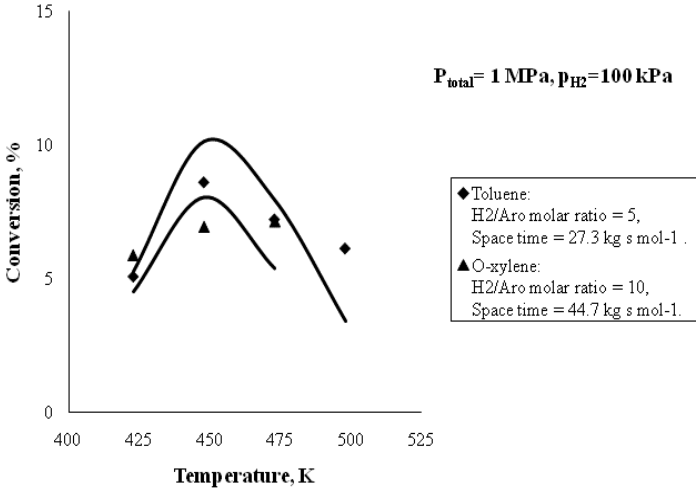

Figure 1. Toluene and o-xylene hydrogenation conversion as a function of the temperature. (symbols: experimental results; lines: obtained from model regression at non-isothermal conditions)

An increase in the hydrogen inlet partial pressure enhances the hydrogenation conversion [5,11]. It results in a corresponding increase of the hydrogen surface concentration and, hence, an enhanced

hydrogenation rate. An opposite effect is observed for the aromatic component inlet partial pressure [5,11]. This can be understood if the corresponding increase in surface concentration of aromatic and partially hydrogenated species significantly hinders the hydrogen chemisorption. The expected increase in hydrogenation because of the higher surface concentrations of the partially hydrogenated intermediates is, in that case, overcompensated by a corresponding decrease in hydrogen surface concentration. As a result a decrease in hydrogenation rate is observed with increasing aromatic component inlet partial pressure.

Hydrogenation single-event Microkinetics

Model construction

A characteristic of aromatic hydrogenation kinetic modeling is that many elementary steps occur in the formation of the cycloalkane out of the aromatic component. In steady-state experimentation no direct information is obtained on these reactive intermediates. In order to construct a kinetic model with a reasonable number of adjustable parameters, information with respect to the surface intermediates was obtained from quantum chemical calculations. Quantum chemical calculation of hydrogenation of benzene on a Pt_{22} cluster suggest that hydrogenation takes place by atomic hydrogen addition according to the Horiuti-Polanyi-type mechanism [15,16]. An aromatic ring is transformed into the corresponding cycloalkane by the consecutive addition of H-atoms. The number of unsaturated nearest carbon atoms to the carbon atom to which the H-atom is being added was found to be one of the distinctive features between the rate and equilibrium coefficients involved in the various H-atom additions. A SEMK model for benzene hydrogenation has been constructed defining reaction families on the basis of the saturation state of nearest neighbor carbon atom [5]. In addition to the saturation state of nearest neighbor carbon atom, the rate and equilibrium coefficients for H-addition are also assumed to depend on the secondary or tertiary character of the carbon atom involved.

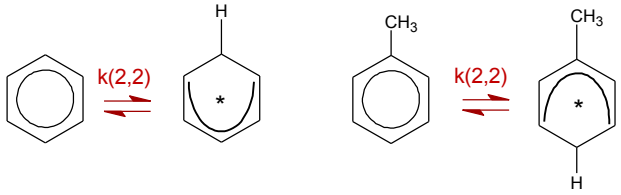

Figure 2. Symmetry effects in hydrogen atom addition.

An additional dependence of the coefficients is related to symmetry effects. This is illustrated in Figure 2, where the first hydrogen atom addition to benzene can occur in 6 equivalent positions whereas the first hydrogen atom addition to toluene has at most 2 equivalent positions. The hydrogenation rate coefficient for an elementary step is written as the product of the number of single-events and the single-event reaction rate coefficient. The latter is assumed to only depend on the saturation state of the nearest neighbors (m= 0,1 or 2) and the degree of branching of the reacting C-atom (n=2 or 3). This results in six different reaction families with specific activation energies and reaction enthalpies.

Unlike in previous Langmuir-Hinshelwood models [1114,16] , no dominant reaction path is considered in this current microkinetic model. This implies that the entire network has to be considered. The reaction network is generated using a computerized algorithm. For benzene hydrogenation by atomic hydrogen, 13 components are interconnected by 20 H-additions and 20 H-abstractions, vide Figure 3. For toluene 40 components are interconnected by 104 H-additions and 104 H-subtractions, while for o-xylene 36 components and 96 H-additions and subtractions are involved. The pseudo-steady state hypothesis is applied for determination of concentration of the partially hydrogenated surface intermediates.

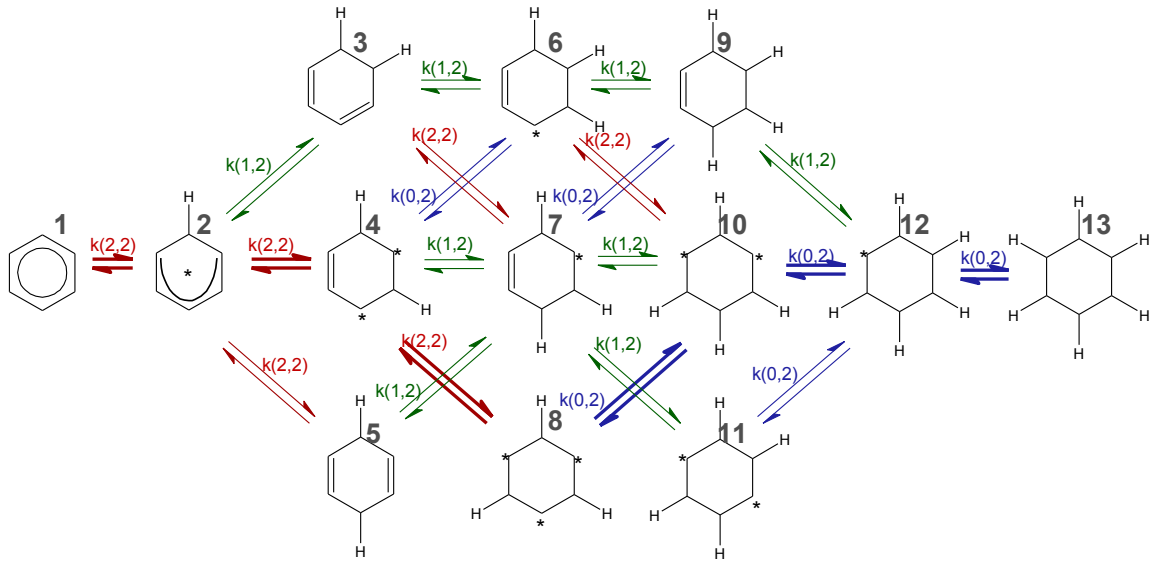

Figure 3. Benzene hydrogenation reaction network indicating the number of the partially hydrogenated intermediates on the catalyst surface as well as the rate coefficients involved in the various hydrogen atom addition reactions [5].

No rate-determining step is assumed. All H-atom additions and abstractions are considered to be non quasi equilibrated. Reactant chemisorption and product desorption was assumed to be quasi equilibrated. The total number of parameters in the model for simultaneous hydrogenation of toluene and o-xylene hydrogenation amounts to 17, i.e., 6 rate coefficients; 6 surface reaction equilibrium coefficients and 5 chemisorption equilibrium coefficients for toluene, methylcyclohane, o-xyne, dimethylcyclohexane and hydrogen. When accounting for their temperature dependence this number doubles to 38, however, order of magnitude calculations have been performed for the preexponential factors of rate, surface reaction equilibrium and chemisorption coefficients. These calculations were based on reasonable assumptions on the mobility of the species involved in the elementary step considered. E.g., aromatic chemisorption was assumed to lead to a significant loss of translational freedom, while the hydrogen mobility on the catalyst surface was assumed to be high. Thermodynamic constraints allow calculating 3 of the surface reaction enthalpies and 2 of the chemisorption enthalpies from the remaining parameter values and the overall reaction enthalpy. Hence 12 adjustable parameters remain to be estimated from regression to experimental data.

The main assumptions in the single-event microkinetic model for aromatic component hydrogenation are summarized below:

1. Competitive dissociative H_2 and molecular aromatic component chemisorption on identical sites.
2. H_2, aromatic component and saturated cycloalkane chemisorption are quasi-equilibrated.
3. No dehydrogenated surface species are considered [17].
4. No rate-determining step or dominant reaction path is assumed.
5. Each reaction step of the network is considered to be reversible.
6. The steady state hypothesis is applied for the partially hydrogenated surface intermediates.
7. The single-event rate coefficients for atomic hydrogen addition only depend on the number of unsaturated nearest neighbor (m) with respect to the carbon atom involved in the hydrogen addition and branching degree (n) of reacting carbon atoms.

The pseudo-steady state hypothesis is applied for the determination of the concentration of the partially hydrogenated surface intermediate. The net production rate (R_j) of any intermediate j is calculated using following expression.

$$R_j = \sum_i r_{i\to j}^{hyd/deh} - r_{j\to i}^{deh/hyd}$$

$$R_j = \sum_i n_{e,i\to j}\left[\tilde{k}_{hyd}(m_i,n_i)C_{H^*} + \tilde{k}_{deh}(m_i,n_i)C_*\right]C_i - n_{e,j\to i}\left[\tilde{k}_{hyd}(m_i,n_i)C_{H^*} + \tilde{k}_{deh}(m_i,n_i)C_*\right]C_j$$

Regression to experimental data

The obtained parameter estimates are in agreement with literature reported values [11,16,12] and lead to a good agreement between experimental observations and model calculations, see Figure 4. The activation energies are in the range of 59 to 73 kJ mol^{-1} and the surface reaction enthalpies correspond to slightly endothermic H addition reactions. This indicates that on Pt the aromaticity is lost upon adsorption of the aromatic component on the surface. Activation energies of the H additions to tertiary carbon atoms were 11 kJ mol^{-1} higher than those to secondary carbon atoms, which can be related to the steric hindrance caused by the methyl group. Chemisorption enthalpies of toluene and o-xylene were estimated very close to each other. As a result, according to the SEMK model, differences in hydrogenation rates between the investigated monoaromatic components are primarily due to differences in H addition rate coefficients rather than in chemisorption strength.

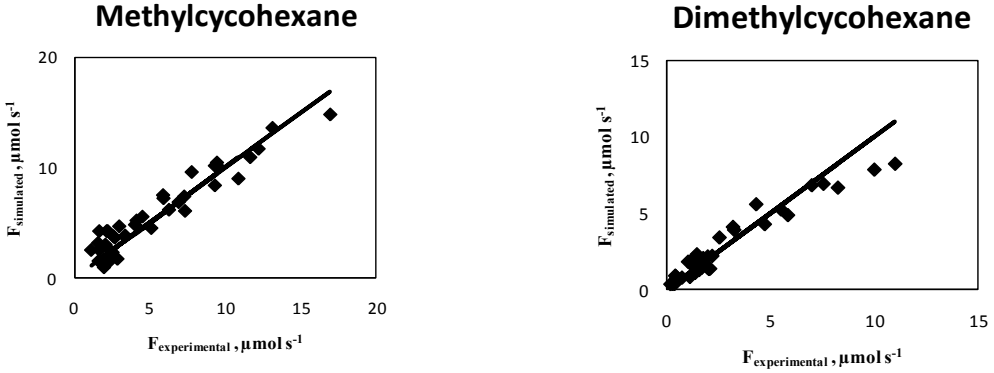

Figure 4. Parity diagram of experimental vs. calculated methylcyclohexane, 1,2-dimethylcyclohexane flow rate. Line: experimental, ♦: obtained from model regression at non-isothermal conditions

As can be observed from Figure 2, the simulated temperature effect is more pronounced than what is actually observed. A refinement in the fundamentals of the pre-exponential factor calculation is expected to further enhance the agreement between model simulations and experimental data.

Conclusions

The single-event methodology has been successfully extended to metal catalysis. The judicious definition of the reaction families has allowed the adequate description of the experimental data using a limited number of adjustable parameters. The single-event hydrogenation rate coefficients are assumed to only depend on the saturation state of the nearest neighbor carbon atoms and the degree of branching of the reacting C-atom. This results in six different reaction families with specific activation energies and reaction enthalpies. Hydrogen additions to tertiary carbon atoms are slower than to secondary carbon atoms due to steric hindrance. Methyl substituent only have a minor effect on the chemisorption characteristics. As a result, differences in aromatic hydrogenation behavior between toluene and o-xylene are mainly governed by differences in hydrogen addition kinetics.

This work demonstrates how single-event microkinetic (SEMK) methodology is a versatile tool in the assessment of hydrocarbon conversion kinetics that can be used in reliable extrapolation towards industrial reactor simulation.

References

[1] Cooper, B. H. and Donnis, B. B. L. (1996), Aromatic saturation of distillates: An overview, *Applied Catalysis A-General*, 137, 203-223.

[2] Vynckier, E., and Froment, G.F., Ed. (1991). Modelling of the kinetics of complex processes based upon elementary steps. *Kinetic and Thermodynamic Lumping of Multicomponent Mixtures,* Amsterdam, Elsevier.

[3] Clymans, P. J. and Froment, G. F.,Computer-Generation of Reaction Paths and Rate-Equations in the Thermal-Cracking of Normal and Branched Paraffins, *Computers & Chemical Engineering*, 8, (1984), 137-142.

[4] Feng, W., Vynckier, E. and Froment, G. F.,Single-Event Kinetics of Catalytic Cracking, *Industrial & Engineering Chemistry Research*, 32, (1993), 2997-3005.

[5] Bera, T., Thybaut, J. W. and Marin, G. B.,Single-Event MicroKinetics of Aromatics Hydrogenation on Pt/H-ZSM22, *Industrial & Engineering Chemistry Research*, In press, doi: 10.1021/ie200541q,

[6] Bos, A. N. R., Lefferts, L., Marin, G. B. and Steijns, M. H. G. M.,Kinetic research on heterogeneously catalysed processes: A questionnaire on the state-of-the-art in industry, *Applied Catalysis A-General*, 160, (1997), 185-190.

[7] Berger, R. J., Stitt, E. H., Marin, G. B., Kapteijn, F. and Moulijn, J. A.,Eurokin - Chemical reaction kinetics in practice, *Cattech*, 5, (2001), 30-60.

[8] Marquardt, D. W.,An Algorithm for Least-Squares Estimation of Nonlinear Parameters, *Journal of the Society for Industrial and Applied Mathematics*, 11, (1963), 431-441.

[9] Boggs, P. T., Byrd, R. H., Rogers, J. E. and Schnabel, R. B.,*NISTIR*, (1992), 92-4834.

[10] Powell, M. J. D., A Hybrid Method for Nonlinear Equations in Numerical Methods for Nonlinear Algebraic Equations, Ed. P Rabinowitz, Gordon and Breach, (1988).

[11] Thybaut, J. W., Saeys, M. and Marin, G. B.,Hydrogenation kinetics of toluene on Pt/ZSM-22, *Chemical Engineering Journal,* 90, (2002), 117-129.

[12] Lin, S. D. and Vannice, M. A.,Hydrogenation of Aromatic-Hydrocarbons over Supported Pt Catalysts .3. Reaction Models for Metal-Surfaces and Acidic Sites on Oxide Supports, J*ournal of Catalysis*, 143, (1993), 563-572.

[13] Vanmeerten, R. Z. C., Degraaf, T. F. M. and Coenen, J. W. E.,Gas-Phase Benzene Hydrogenation on a Nickel-Silica Catalyst .3. Low-Field Magnetization Measurements on Hydrogen, Benzene, Cyclohexene and Cyclohexane Adsorption, and Benzene Hydrogenation, *Journal of Catalysis*, 46, (1977), 1-12.

[14] Lindfors, L. P., Salmi, T. and Smeds, S.,Kinetics of Toluene Hydrogenation on Ni/Al2O3 Catalyst, Chemical Engineering Science, 48, (1993), 3813-3828.

[15] Saeys, M., Reyniers, M. F., Neurock, M. and Marin, G. B.,Ab initio reaction path analysis of benzene hydrogenation to cyclohexane on Pt(111), *Journal of Physical Chemistry B*, 109, (2005), 2064-2073.

[16] Saeys, M., Reyniers, M. F., Thybaut, J. W., Neurock, M. and Marin, G. B.,First-principles based kinetic model for the hydrogenation of toluene, J*ournal of Catalysis*, 236, (2005), 129-138.

[17] Saeys, M., Reyniers, M. F., Marin, G. B. and Neurock, M.,Density functional study of benzene adsorption on Pt(111), *Journal of Physical Chemistry B*, 106, (2002), 7489-7498.